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COMMUNICATION

CATIONIC CARBONYL COMPLEXES OF MANGANESE (I) WITH NITRILES AND DINITRILES

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ABSTRACT The reaction of $Mn(CO)_5OClO_3$ with nitriles,L, and dinitriles,L-L,in a wide variety of conditions affords cationic pentacarbonyls, $[Mn(CO)_5(L)]ClO_4$ and $[Mn(CO)_5(L\text{-}L)]ClO_4$ and fac-tricarbonyls, $[Mn(CO)_3(L)_3]ClO_4$ and $[(CO)_3Mn(\mu\,L\text{-}L)_3Mn(CO)_3](ClO_4)_2$

RESULTS AND DISCUSSION The reaction of $Mn(CO)_5OClO_3$ with nitriles,(1/3 molar ratio) in refluxing $CHCl_3$ gave cationic tricarbonyl derivatives fac-$[Mn(CO)_3(L)_3]ClO_4$[1], (L: EtCN, $CH_2{=}CHCH_2CN$, PhCN, $PhCH_2CN$). In CH_2Cl_2 at room temperature the reaction gave a mixture of pentacarbonyls $[Mn(CO)_5(L)]ClO_4$ (which are initially formed) and the tricarbonyls fac-$[Mn(CO)_3(L)_3]ClO_4$; from the resulting solutions pure pentacarbonyls were isolated in low yield; by using equimolecular ratio, at -10°C, the formation of fac-tricarbonyl was greatly reduced, but the yields were not improved due to the low solubility of the precursor neutral perchlorate. All attempts to promote further substitution have failed; use of EtOH as solvent led to the formation of a fac-tricarbonyl derivative, possibly fac-$[Mn(CO)_3(EtOH)_3]ClO_4$, not previously described, which could not be characterized since it was obtained as an oil by solvent evaporation; IR (cm^{-1}) ν CO (CH_2Cl_2) 2040 s, 1935 br,s.

Similar reactions with dinitriles L-L, (L-L: $NCCH_2CN$, $NCCH_2CH_2CN$, $NCCH_2CH_2CH_2CN$, $o\text{-}C_6H_4(CN)_2$), in CH_2Cl_2 at room temperature in 1/3 ratio led to precipitation of white-yellow solids, identified by IR spectroscopy as mixtures of the corresponding penta- and tricarbonyl derivatives. Attempts to separate pure pentacarbonyls by succesive recrystallizations were unsuccesful, although analytical data are very close to the expected for $[Mn(CO)_5(L\text{-}L)]ClO_4$. The $Mn(CO)_5OClO_3$ reacted with a three fold excess of dinitriles L-L in refluxing $CHCl_3$ giving, through the intermediate pentacarbonyls, the tricarbonyls fac-$[(CO)_3Mn(\mu\ L\text{-}L)_3Mn(CO)_3](ClO_4)_2$, which must be dimers in accordance with conductivity data at various concentrations, and their structures are probably those in which the dinitriles are bridging two $Mn(CO)_3$ groups.

The pentacarbonyls show four ν CO bands in CH_2Cl_2 or in $CHCl_3$. Although uncommon, since IR spectra of pentacarbonyls usually exhibit only three absorptions ($2\,A_1 + E$) in the ν CO region, this behaviour is not unique and some pentacarbonyls can be found in the literature with four ν CO bands[2]. Using the Cotton-Kraihanzel method[2], the B_1 band which is not IR active for rigorous C_{4v} symmetry, must appear at 2106 cm^{-1} which supports the view that the band at 2122 cm^{-1} may be the B_1 mode. The weak ν CN absorptions of coordinated nitriles, at higher wavenumbers than that of free ligands, indicate that all the nitriles and dinitriles are bound to the metal through the nitrogen.

EXPERIMENTAL All the reactions were carried out under N_2 and in absence of light.

Preparation of $[Mn(CO)_5(L)]ClO_4$ (General method) A mixture of $Mn(CO)_5OClO_3$[3] in

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CH_2Cl_2, obtained from 0.3 g (1.09 mmol) of $Mn(CO)_5Br$, and L was stirred. The yellow oil which results from the removal of the solvent in vacuo, was washed with Et_2O to extract the unreacted L and the fac-$[Mn(CO)_3(L)_3]ClO_4$. The resulting solid was recrystallized from $CH_2Cl_2/EtOH$. IR (cm^{-1}) $\bar{\nu}$ CO (CH_2Cl_2 or $CHCl_3$) 2165 w, 2122 w, 2080 s, 2045 m, for all the pentacarbonyls. The specific conditions for each reaction (neutral perchlorate/ligand mol ratio, solvent, time, temperature and yield), analytical and conductivity data for the cationic pentacarbonyls were as follows:

L: EtCN, 1/2.5, $CHCl_3$, 8 h, room temperature, 39%. M.P. 87°C. Λ_M 92 S cm^2 mol^{-1}. (The solvent used for all conductivity measurements was $MeNO_2$). $\bar{\nu}$ CN (nujol) 2315 cm^{-1}. Found C 27.49, H 1.59, N 3.97. Calc. C 27.49, H 1.44, N 4.00 %. L: $CH_2{=}CHCH_2CN$, 1/2.2, $CHCl_3$, 9 h, room temperature, 21%. M.P. 96°C. Λ_M 93 S cm^2 mol^{-1}. $\bar{\nu}$ CN (nujol) 2310 cm^{-1}. Found C 29.20, H 1.41 N 3.31. Calc. C 29.30, H 1.39, N 3.87%. L: $PhCH_2CN$, 1/1, CH_2Cl_2, 33 h, -10°C, 25%. M.P. 92°C. Slope 143[4]. $\bar{\nu}$ CN (nujol) 2317 cm^{-1}. Found C 38.55, H 1.82, N 3.78. Calc. C 37.94, H 1.71, N 3.40%.

Preparation of $[Mn(CO)_3(L)_3]ClO_4$ L: EtCN. To a solution of $Mn(CO)_5OClO_3$ (prepared from 0.3 g, 1.09 mmol, of $Mn(CO)_5Br$) in 40 cm^3 of $CHCl_3$, 0.2 cm^3 (2.49 mmol) of EtCN was added. After refluxing 2 h, the solvent was removed under reduced pressure. The residue was washed with hexane to extract unreacted L. Yield 65%. M.P. 98°C. Slope 200[4]. IR (cm^{-1}) $\bar{\nu}$ CO (CH_2Cl_2) 2070 s, 1977 br,s; $\bar{\nu}$ CN (nujol) 2300. Found C 35.06, H 3.63, N 10.17. Calc. C 35.71, H 3.74, N 10.40%. L: PhCN. It was obtained by the procedure above described. Yield 65%. M.P. 97°C. Λ_M 93 S cm^2 mol^{-1}. IR (cm^{-1}) $\bar{\nu}$ CO ($CHCl_3$) 2070 s, 1983 br,s; $\bar{\nu}$ CN (nujol) 2270. Found C 53.12, H 2.79, N 7.67. Calc. C 52.62, H 2.76. N 7.50%. L: $CH_2{=}CHCH_2CN$ and $PhCH_2CN$. They were not characterized because of the formation of uncrystallizable oils. Their IR spectra (CH_2Cl_2) in the $\bar{\nu}$ CO region are the same (cm^{-1}) 2070 s, 1985 br,s.

Preparation of fac-$[(CO)_3Mn(\mu\ L\text{-}L)_3Mn(CO)_3](ClO_4)_2$ L-L: $NCCH_2CH_2CN$. A mixture of $Mn(CO)_5OClO_3$ (from 0.25 g (0.91 mmol) of $Mn(CO)_5Br$) in 50 cm^3 of $CHCl_3$ and 0.218 g (2.73 mmol) of $NCCH_2CH_2CN$ was refluxed for 18 h. The resulting oil was washed with CH_2Cl_2 and Et_2O. Yield 50%. Recrystallized from Me_2CO/Et_2O. It blackens at 188°C without melting. Slope 316[4]. IR (cm^{-1}) $\bar{\nu}$ CO (Me_2CO) 2065 s, 1983 br,s; $\bar{\nu}$ CN (nujol) 2310. Found C 30.09, H 1.70, N 11.70. Calc. C 30.15, H 1.69, N 11.72%. L-L: $o\text{-}C_6H_4(CN)_2$. It was prepared using a similar procedure. Yield 38%. It blackens at 193°C. Slope 367[4]. IR (cm^{-1}) $\bar{\nu}$ CO (Me_2CO) 2075 s, 1955 br,s; $\bar{\nu}$ CN (nujol) 2275. Found C 42.09, H 1.17, N 9.53. Calc. 41.82, H 1.40, N 9.75%. For L-L: $NCCH_2CN$ and $NCCH_2CH_2CH_2CN$ the complexes could not be purified.

NOTES AND REFERENCES

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4.- Slope of the straight line which results from plotting $\Lambda_0 - \Lambda_e$ versus $\sqrt{Ce}$, where Λ_e is the equivalent conductivity, Λ_0 is Λ_e at infinite dilution, and Ce is the equivalent concentration. The value 143 and 200 are in the expected range for 1:1 electrolytes and the values 316 and 367 are in the expected range for 1:2 electrolytes when $MeNO_2$ is used as solvent.- R.D. Feltham and R.G. Hayter, J. Chem. Soc. 1964, 4587